

INCREASING THE WET SLIPPAGE PROPERTIES OF TEXTILE MATERIAL, AND WET-ACTING LUBRICANTS FOR THIS PURPOSE

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In the treatment of textile material in the form of textile piece goods, particularly in rope form or tubular form, essentially during pre-treatment, dyeing, optical brightening or after-treatment, in aqueous liquor under such conditions that transport folds can form in the textile substrate or abrasion can take place of substrate to adjacent substrate or apparatus parts – in particular in jet dyeing machines and in winch becks –, undesired phenomena are the marking of the transport folds and the formation and marking of chafe points, which then, as unlevel features, impair the fabric appearance and possibly also the physical properties of the treated goods and consequently of the finished goods. In order to counter these interfering phenomena, wet-acting lubricants (i.e. wet acting slip agents), which reduce the tendency toward the formation or stabilisation and consequently the marking of folds, in particular transport folds, and reduce the substrate/substrate and substrate/metal friction and consequently the tendency toward the formation and marking of chafe points, are employed in the corresponding process steps. It has already been proposed to employ wax dispersions of different types as lubricants (or slip agents) for avoiding the formation of transport folds or creases, e.g. as described in GB-A-2128202 or 2282153. In EP-A-506613 there are described for a similar purpose compositions containing polymers of the radicalic polymerisation of ethylenically unsaturated monomers (especially acrylic polymers) in admixture with esters of polyols with a C₈₋₂₆-fatty acid. In WO-A-85/03959 there are described certain waterless compositions comprising higher alkyl esters of benzene-mono- to hexa-carboxylic acid [which in that document are designated as "polyesters" – in the examples there being illustrated trioctyl-, triisooctyl- and tri-(2-ethyl-hexyl)-trimellitate] and some further components (monoesters, diesters, ethoxylated alcohols and esters of ethoxylated alcohols), which may also be diluted with water and be used as dyeing assistants. In US-A-5820982 there is described the production of certain polyester resins from recycled polyterephthalate (in the examples polyethyleneterephthalate) and a sulphonyldicarboxylate (in the examples sulphonyisophthalate) with glycol and oxyalkylated polyol, which may be terminated with a polyacid (in the examples trimellitic acid or hypophosphoric acid), to give a polyester resin useful for various purposes, in particular as a size for fibres and as a levelling agent – in the sole application example (Example 8) there is illustrated the use as a levelling agent in the dyeing of a yarn package.

In the constant refinement of the processes and machines with the aim of increasing the output and an environmentally acceptable procedure, machines and processes are being developed which are designed for higher speeds or higher outputs and/or which work with shorter liquor ratios. Greater demands are thus also made of the lubricants employed. Thus, for example, they must be resistant to

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particularly high shear forces while developing their action as well as possible for short liquors too. The shorter the liquor, the greater the requisite efficacy of the respective treatment agents since wet slippage of the goods and the achievement of a level, smooth goods appearance without damage to the goods is made more difficult the greater the proportion of liquor taken up by the goods.

It has now been found that certain end-capped polyesters having a certain hydrophilicity, as is sufficient for the polyester to be dispersible or colloiddally soluble in water, in particular self-dispersible or colloiddally soluble, particularly also end-capped polyesters as otherwise used as soil release agents, surprisingly have an advantageous action as wet-acting lubricants (i.e. as wet-acting slip agents) in the treatment of textile piece goods in rope form or tubular form, particularly made from polyester fibres, in jet dyeing machines, where, for example, they do not hinder or impair the dyeing, but act surprisingly well and extremely superficially on the wet substrate as wet-acting lubricants in surprisingly high efficiency and yield, and further with a high degree of constancy and reproducibility of these properties, even if the products employed come from different lots and/or have been stored for a prolonged time.

The invention relates to the use of such polyesters (P_S) as defined below, as wet-acting lubricants for the treatment of textile material in the form of textile piece goods, particularly in rope form or tubular form, to the corresponding wet-acting lubricants, and to their production and aqueous compositions (W) thereof.

A first subject-matter of the invention is thus the use of

(P_S) water-dispersible or -colloiddally soluble, end-capped polyesters

as wet-acting lubricants in the treatment of textile piece goods with a textile treatment agent (T) by an exhaust process from aqueous liquor under conditions which would otherwise in the textile substrate favour the formation of transport folds and/or the occurrence of friction in or on the substrate,

or respectively is

a process for the treatment of textile piece goods with a textile treatment agent (T) by exhaust methods from aqueous liquor under conditions which would otherwise in the textile substrate favour the formation of transport folds and/or the occurrence of friction in or on the substrate, characterized in that the process is carried out in the presence of a water-dispersible or -colloiddally soluble end-capped polyester (P_S) as a wet-acting lubricant.

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The end-capped polyesters (P_S) are in particular end-capped polyesters that are polymers obtainable by polymerisation/polyesterification reaction of corresponding esterifiable monomers (in particular hydroxy- substituted monomers and/or monomers substituted with carboxy or a suitable functional derivative of carboxy) and end-capping esterification reaction. As end-capped polyesters (P_S), it is possible to employ known polyesters or polyesters which can be produced analogously to known polyesters. For the production of the end-capped polyesters (P_S), it is advantageous to use starting materials – in particular monomers suitable for the formation of polyester chains by polycondensation and/or, in the case of lactones, also polyaddition polymerisation reaction – which are suitable for the formation of linear polyester chains, in particular difunctional compounds (D) which are monomers suitable for polyesterification (i.e. polymerisation by esterification), and monofunctional compounds (E) which are suitable for the end capping of the polyesters, and optionally higher oligo-functional compounds (H) which are suitable for the branching of the polyesters. The polyesters (P_S) to be employed in accordance with the invention are dispersible (preferably self-dispersible) or colloiddally soluble in water and contain in the respective molecule at least one hydrophilic constituent and at least one hydrophobic constituent, so that the polyester formed has a corresponding hydrophilicity, so as to be dispersible or colloiddally soluble, in particular self-dispersible or at most colloiddally soluble, in water. The mono-, di- and higher oligo-functional compounds are essentially carboxylic acids or suitable functional derivatives thereof, principally esters of low-molecular-weight alcohols which can be cleaved off by transesterification, particularly esters of C_{1-4} -alcohols, for example ethyl esters or preferably methyl esters, or anhydrides, on the one hand, and hydroxyl compounds, in particular alcohols, on the other hand, which, through esterification or transesterification, result in corresponding carboxylic acid ester groups, or also lactones of hydroxycarboxylic acids, and may optionally contain one or more heteroatomic bridging members, for example $-O-$, $-CO-$, $-CO-O-$, $-NH-CO-O-$, $-CO-N-$, $-CO-NH-$, $-NH-CO-NH-$ or $-SO_2-$.

Suitable as difunctional monomers (D) are, in particular,

(A) aliphatic or araliphatic diols, in particular

(A₁) aliphatic and araliphatic diols which otherwise contain no hydrophilic constituents or substituents, in particular alkanediols having 2 to 10 carbon atoms, where the alkane radical may be linear or, if it contains 3 to 10 carbon atoms, alternatively branched, or, if it contains 4 to 10 carbon atoms, alternatively cyclic, di(C_{1-2} -hydroxyalkyl)benzenes, water-insoluble polyether-diols, polyester-diols, polycarbonate-diols, polyurethane-diols and polyesterurethane-diols,

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and (A₂) aliphatic or araliphatic diols which contain at least one hydrophilic constituent and/or at least one hydrophilic substituent, principally water-soluble polyalkylene glycols (in particular polyethylene glycols, oligopropylene glycols and copolyethylene-propylene glycols) and polyetherurethane-diols, aliphatic or araliphatic sulpho group-containing diols which contain one or more, for example one or two, sulpho groups, and aliphatic or araliphatic carboxyl group-containing diols which contain one or more, for example one or two, carboxyl groups in alkali metal salt form;

(B) aliphatic, aromatic or araliphatic dicarboxylic acids, in particular

(B₁) alkanedicarboxylic acids having 2 to 10 carbon atoms in the alkane radical, where, if the alkane radical contains 4 to 10 carbon atoms, it may optionally be interrupted by oxygen, aromatic dicarboxylic acids having one to three benzene rings, two of which may optionally be fused, or araliphatic dicarboxylic acids which contain 9 to 18 carbon atoms and contain one benzene ring or two optionally fused benzene rings, where aromatic rings may be bonded to further aliphatic, aromatic or araliphatic parts of the molecule, optionally via oxygen, or may be bonded to a further aromatic part of the molecule, optionally via a sulphone group, or functional derivatives thereof (e.g. C₁₋₄-alkyl esters of the dicarboxylic acids or optionally their anhydrides),

and (B₂) aliphatic, aromatic or araliphatic dicarboxylic acids which contain at least 4 carbon atoms and in which the hydrocarbon radical to which at least one of the two carboxyl groups is bonded contains 1 to 14 carbon atoms, and which contain at least one hydrophilic radical (for example a hydrophilic polyethylene glycol ether chain) and/or at least one hydrophilic substituent (for example one or more, in particular one or two, sulpho groups) in the molecule, or functional derivatives thereof (e.g. C₁₋₄-alkyl esters of the dicarboxylic acids or optionally their anhydrides);

(C) aliphatic hydroxymonocarboxylic acids, in particular

(C₁) aliphatic unsubstituted hydroxycarboxylic acids having 3 to 18 carbon atoms, optionally in lactone form, or prepolymers (polyesters) thereof. e.g. on a starting diol such as e.g. those mentioned above as (A₁).

Sulpho group-containing monomers (D) are difunctional in so far as sulpho groups substantially do not undergo esterification under the reaction conditions required for esterification of the carboxy groups or respectively for transesterification their lower alkyl esters.

As (A₁), mention may be made, for example, of ethylene glycol, 1,3-propanediol, 2,4-dimethyl-2-ethylhexane-1,3-diol, 2,2-dimethyl-1,3-propanediol, 2-ethyl-2-butyl-1,3-propanediol, 2-ethyl-2-iso-

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butyl-1,3-propanediol, 1,3-butanediol, 1,4-butanediol, 1,5-pentanediol, 1,6-hexanediol, 2,2,4-trimethyl-1,6-hexanediol, 1,2-, 1,3- or 1,4-cyclohexanedimethanol, 2,2,4,4-tetramethyl-1,3-cyclobutanediol, para-xylylenediol, 1,2-propylene glycol, neopentyl glycol, polytetrahydrofurans, higher propylene glycols (having > 10 monomer units), polycaprolactones from the addition of an ϵ -caprolactone onto an alkanediol (for example onto one of the above-mentioned alkanediols), or polycarbonate-diols from the above-mentioned alkanediols. Of the diols (A_1), preference is given to C_{2-4} -alkanediols, in particular propylene glycol, ethylene glycol and combinations of propylene glycol and ethylene glycol.

As (A_2), mention may be made, for example, of the following:

(A_{21}) polyethylene glycols (for example having an average molecular weight \overline{M}_w in the range from 200 to 10,000, preferably 500 to 5000), water-soluble oligopropylene glycols (having ≤ 10 monomer units),

(A_{22}) alkanediols having 4 to 10 carbon atoms and which carry one or two sulpho groups as substituents, and are optionally oxyethylated and/or oxypropylated, benzenedimethanols which carry a sulpho group as substituent on the benzene ring, for example 2-sulphobutanediol and products of the addition reaction thereof with ethylene oxide and optionally propylene oxide, sulpho-1,2-benzenedimethanol (sulphoxylene glycol) and sulpho-1,4-benzenedimethanol, or additionally sulphonated diepoxides of alkanediols or polyethylene glycols (for example from the reaction of the respective alkanediols or polyethylene glycols with epichlorohydrin and sulphonation with a bisulphite, for example with sodium bisulphite) and sulphonated oxyalkylated alkenediols (for example from the sulphonation of the product of the addition reaction of oxiranes – principally ethylene oxide and/or propylene oxide – onto alkenediols with sulphite, for example with sodium sulphite),

or also (A_{23}) monoamidation products of di- or higher carboxylic acids [for example those of type (B_1) or (H_2) below] with low-molecular-weight dialkanolamines, for example with diethanolamine, dipropanolamine or diisopropanolamine, where the non-amidated carboxyl groups are in alkali metal salt form (particularly as Na, Li or K salt).

Of the diols (A_2), those of the type (A_{21}) are preferred, especially polyethylene glycols.

As (B_1), mention may be made, for example, of the following: adipic acid, succinic acid, glutaric acid, pimelic acid, suberic acid, azelaic acid, sebacic acid, maleic acid, fumaric acid, dimethylmalonic acid, diglycolic acid, 3,3'-oxydipropionic acid, trimethyladipic acid, itaconic acid, orthophthalic acid, isophthalic acid, terephthalic acid, oxydibenzoic acid, naphthalene-2,6-dicarboxylic acid, naphthalene-1,8-dicarboxylic acid, naphthalene-1,4-dicarboxylic acid, 1,2-di-(p-carboxyphenoxy)-ethane, 1,2-di-(p-carboxyphenyl)-ethane, biphenyl-2,2'-dicarboxylic acid, 1,4-cyclohexanedicarboxylic acid

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and 4,4'-dicarboxydiphenyl sulphone, and their methyl esters. Of the aliphatic dicarboxylic acids (B_1), preference is given to the α,ω -dicarboxylic acids; of the aliphatic, aromatic and araliphatic dicarboxylic acids (B_1), preference is given to the aromatic ones, particularly terephthalic acid.

As (B_2), mention may be made, for example, of the following: sulphosuccinic acid, methylsulphosuccinic acid, sulphomethylsuccinic acid, 4-sulphophthalic acid, 5-sulphoisophthalic acid, dimethylsulphoisophthalic acid, sulphoterephthalic acid, sulphomalonic acid, 1,3-dimethyl 5-(p-sulphophenoxy)-isophthalate, phenyl-3,5-dicarboxy-benzenesulphonic acid, 2,6-dimethylphenyl-3,5-dicarboxybenzenesulphonic acid, naphthyldicarboxylic acid benzenesulphonic acid, sulpho-4-naphthalene-2,7-dicarboxylic acid, sulphobis(hydroxycarbonyl)-4,4'-diphenyl sulphone and products of the sulphonation of oligoesters of unsaturated dicarboxylic acids obtainable by reaction thereof, for example, with sodium sulphite, for example on the basis of maleic acid, itaconic acid or citraconic acid, for example with the above-mentioned alkanediols, and polyoxyalkylenedicarboxylic acids, for example from the carboxymethylation of polyalkylene glycols or from the catalytic or electrochemical oxidation of the terminal $\text{CH}_2\text{-OH}$ groups of polyalkylene glycols to COOH groups, where the polyalkylene glycols are preferably polyethylene glycols and/or polypropylene glycols, and methylesters of the dicarboxylic acids. Of the sulpho group-containing acids (B_2), 5-sulphoisophthalic acid is especially preferred; of the acids (B_2), the sulpho group-free ones are preferred, especially the polyethylene glycol ether chain-containing ones.

As (C_1), mention may be made, for example, of the following: glycolic acid, hydroxypropionic acid, 12-hydroxystearic acid, 2-hydroxycaproic acid, 3- or 4-hydroxybutyric acid, ϵ -caprolactone, γ -butyrolactone and 3,3-dimethyl-4-butyrolactone, and prepolymers thereof.

Suitable monofunctional compounds (E) for the end capping of the polyesters are expediently hydroxy- or carboxy-substituted compounds capable of esterification with a carboxy or respectively hydroxy group of the not yet end-capped polyester, where the carboxy group may also be in the form of a suitable functional derivative, e.g. a C_{1-4} -alkyl ester of the carboxylic acid; for example,

- (E₁) simple alcohols or carboxylic acids or their methyl esters, which do not contribute towards the hydrophilicity of the polyester,
 - and (E₂) hydroxyl or carboxyl compounds or their methyl esters, which may contribute towards the hydrophilicity of the polyesters, particularly those which contain hydrophilic polyalkylene glycol ether chains and/or carry one or two sulpho groups as substituents,
- and which have a boiling point which is expediently higher than the (trans)esterification temperature.

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Suitable as (E₁) are, in particular,

- (E₁₁) simple aliphatic or araliphatic alcohols, for example C₄₋₆-alkanols and phenylalkanols,
and (E₁₂) simple aliphatic, araliphatic or aromatic monocarboxylic acids, for example butanoic acid
and optionally alkyl-substituted benzoic acids, or their methyl ester.

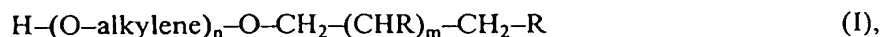
Suitable as (E₂) are, in particular,

- (E₂₁) aliphatic or araliphatic hydroxyl compounds which contain a hydrophilic moiety, for
example a polyalkylene glycol ether chain, and/or carry one or more sulpho groups as
substituents,
and (E₂₂) aliphatic, araliphatic or aromatic, carboxyl group-containing, hydrophilic compounds or
their methyl esters, which contain a hydrophilic moiety, for example a polyalkylene glycol
ether chain, and/or carry one or more sulpho groups as substituents.

As (E₁₁), mention may be made, for example, of the following: cyclohexanol, benzyl alcohol and
(C₁₋₄-alkyl)-benzyl alcohol.

As (E₁₂), mention may be made, for example, of the following: benzoic acid and butyric acid.

As (E₂₁), mention may be made, for example, of the following: adducts of ethylene oxide and/or
propylene oxide, and optionally butylene oxide or styrene oxide, onto an aliphatic monoalcohol having
1 to 18 carbon atoms or onto an alkylphenol having a total of 10 to 24 carbon atoms, where at least 50
mol-% of the alkyleneoxy groups present are advantageously ethyleneoxy groups, and the incorporated
polyalkylene glycol ether chains are preferably those consisting exclusively of ethyleneoxy units (for
example up to an average molecular weight in the range from 200 to 20,000, particularly from 200 to
5000), and aliphatic and/or araliphatic hydroxyl compounds which carry one or two sulpho groups as
substituents and optionally contain oxyethylene and/or oxypropylene groups in the molecule. Of these,
adducts of ethylene oxide onto a low-molecular-weight alkanol (in particular C₁₋₄-alcohol) are
preferred. Sulpho group-containing compounds of type (E₂₁) which are particularly worthy of mention
are 2-hydroxyethanesulphonic acid, 2-hydroxypropanesulphonic acid, 4-(2-hydroxyethoxy)-benzene-
sulphonic acid and compounds of the average formula



in which alkylene denotes ethylene and/or 1,2-propylene,
R denotes hydrogen or SO₃H,

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m denotes 0 or 1
 and n denotes a number in the range from 1 to 30,
 where at least one of the m+1 symbols R denotes SO₃H.

As (E₂₂), mention may be made, for example, of the following: carboxymethylation products of the adducts of ethylene oxide and/or propylene oxide onto an aliphatic monoalcohol having 1 to 18 carbon atoms, where at least 50 mol-% of the alkyleneoxy groups present are advantageously ethyleneoxy groups and the incorporated polyalkylene glycol ether chains preferably consist exclusively of ethyleneoxy units (for example up to an average molecular weight in the range from 200 to 5000), or products of the catalytic or electrochemical oxidation of the terminal -CH₂-OH groups of such addition products to give terminal -COOH groups, or aliphatic, araliphatic or aromatic carboxylic acids having 7 to 22 carbon atoms which carry a sulpho group as substituent, for example ortho-, meta- or para-sulphobenzoic acid or sulphonated oleic acid (for example from the reaction of oleic acid with sodium sulphite). Of said compounds (E₂₂), the sulpho group-free ones are preferred.

Sulpho group-containing reactants (E₂₁) and (E₂₂) are grouped here with monofunctional compounds in so far as sulpho groups substantially do not undergo esterification under the reaction conditions required for esterification of the carboxy groups or respectively for transesterification their lower alkyl esters.

Of the components (E₁) and (E₂), the components (E₂) are preferred, particularly (E₂₁), especially the non-ionogenic ones.

Suitable as (H) are tri- and higher oligo-functional compounds which can lead to branched products with ester formation, in particular

- (H₁) compounds containing 3 to 10 alcoholic hydroxyl groups,
 - (H₂) compounds containing 3 or more, for example 3 or 4, carboxyl groups, or a functional derivative thereof (e.g. a C₁₋₄-alkyl ester of the carboxylic acids or optionally their anhydrides),
- and (H₃) hydroxycarboxylic acids containing at least 2 carboxyl groups and/or at least 2 hydroxyl groups and functional derivatives thereof (e.g. C₁₋₄-alkyl esters of the carboxylic acids or optionally, if they contain at least 2 carboxyl their anhydrides),.

Suitable as (H₁) are, for example, tri- to hexahydroxyalkanes, for example having 3 to 6 carbon atoms, for example pentaerythritol, trimethyloethane, trimethylolpropane, glycerol, mannitol, sorbitol and

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1,2,3-hexanetriol, and oxyalkylation products thereof, particularly oxyethylation and/or oxypropylation products, for example having 1 to 20 oxyethylene groups and optionally 1 to 10 oxypropylene groups.

As oligocarboxylic acids (H_2), use can be made of aliphatic, araliphatic or preferably aromatic compounds, for example having 6 to 15 carbon atoms, preferably benzenetricarboxylic acids (in particular trimellitic acid, hemimellitic acid or trimesic acid) or their methyl esters.

Suitable hydroxycarboxylic acids (H_3) are aromatic compounds or also aliphatic compounds, for example aromatic benzene-based dicarboxylic acids which carry a hydroxyl group on the benzene ring, for example hydroxy-4- or -5-isophthalic acid, or aliphatic saturated dicarboxylic acids having 4 to 8 carbon atoms, for example hydroxy-2-methylsuccinic acid, hydroxymethylglutaric acid and hydroxyglutaric acid, or aliphatic saturated carboxylic acids having 3 to 8 carbon atoms, which may carry 2 to 6 hydroxyl groups, in particular ascorbic acid, gluconic acid and glucoheptonic acid, or methyl esters thereof, or also products of the partial amidation of tri- or higher functional carboxylic acids [for example those of type (H_2)] with low-molecular-weight mono- or dialkanolamines, for example with mono- or diethanolamine, -propanolamine or -isopropanolamine, or additionally products of the monoamidation of dicarboxylic acids [for example those of type (B_1)] with low-molecular-weight dialkanolamines, for example with diethanolamine, dipropanolamine or diisopropanolamine, where the non-amidated carboxyl groups are in the form of the free acid.

For the production of the polyesters (P_3) to be employed in accordance with the invention, there may in particular be polymerised (A) with (B) and optionally (C), or (C) alone optionally on a starter molecule (A) or (B), and optionally with (A) or (B), and optionally with (H), end capping being carried out with (E). It is advantageous to employ difunctional compounds, in particular diols (A), which are reacted with corresponding dicarboxylic acids, in particular of type (B) or functional derivatives thereof and optionally with hydroxycarboxylic acids of type (C), or products of the polymerisation of hydroxycarboxylic acids (or lactones thereof), in particular of type (C), which are optionally reacted further with (poly)esters of diols, in particular of type (A) with corresponding dicarboxylic acids, in particular of type (B), or functional derivatives thereof. Monofunctional compounds of type (E) are employed in order to cap an end group (hydroxyl or carboxyl group). If desired, higher oligo-functional compounds, for example of type (H), can be employed in order to produce branched polyesters. The relative amounts or molar ratios of the respective starting compounds are advantageously selected in such a way that the polyesters produced therefrom have the desired hydrophilicity properties, i.e. in particular in such a way that the polyesters, besides a hydrophobic moiety, also have a hydrophilic moiety, which can be controlled, in particular, through a suitable choice of corresponding starting

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compounds. Thus, for example, hydrophobic moieties are built up by polyesterification with diols of type (A_1), with dicarboxylic acids of type (B_1) and/or respectively with hydroxymonocarboxylic acids of type (C_1), while hydrophilic moieties are introduced with components of type (A_2) or (B_2). A contribution towards the hydrophilicity of the polyesters is also made with compounds of type (E_{21}) and (E_{22}).

The esterification reaction (or transesterification reaction if carboxylic acid esters of alcohols, which can be cleaved off under esterification conditions, are transesterified) can be carried out in a manner known per se, with the respective selected components (D) and (E) and optionally (H) being reacted, with addition of suitable catalysts, at elevated temperature, for example in the range from 150 to 280°C, preferably from 160 to 260°C. If diols (A) are employed, it is advantageous first to employ the more volatile and not to add the less volatile for the further esterification until the esterification of the former has begun or progressed. The esterification (or transesterification) can initially be carried out under atmospheric pressure, for example in the presence of inert solvents or preferably in the absence of any solvents, in which case volatile by-products, for example unreacted starting materials and other volatile accompanying substances, can then be removed under reduced pressure. Suitable transesterification and condensation catalysts are, for example, conventional compounds of polyvalent metals, for example titanium tetraisopropoxide, manganese(II) acetate, dibutyltin oxide or antimony trioxide/-calcium acetate, which can be employed in the concentrations which are usual per se, for example in the range from 0.0005 to 1 % by weight, particularly from 0.002 to 0.1 % by weight, based on (P_S).

The hydrophilic starting compounds may, for example, be exclusively those which contain as hydrophilic moieties polyethylene glycol ether chains, which are suitable or preferred for the production of non-ionogenic polyesters, or exclusively those which contain sulfo groups as hydrophilic substituents, which are suitable or preferred for the production of anionic polyesters, or also a combination of the two.

The respective molar ratios are advantageously selected in such a way that an excess of hydroxyl compounds over carboxyl compounds is employed overall, depending on the volatility of the diols employed, and advantageously in such a way that any carboxyl groups are capped with mono-functional alcohols, preferably those of type (E_{21}). If higher oligo-functional compounds of type (H) are employed, their molar ratio to the difunctional compounds (D) employed is advantageously kept low. It is in particular advantageous to select the respective molar ratios in such a way that no significant crosslinking takes place, principally in such a way that aqueous dilution of the product does not form gelatinous, irreversible agglomerates, but instead a dispersion or colloidal solution. If, for

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example, the starting materials are diols (A_1) and (A_2), dicarboxylic acids (B_1) (or diesters thereof), a polyol (H_1) and a monofunctional compound (E_{21}), it is advantageous to employ ≤ 1 mole equivalent, preferably ≤ 0.5 mole equivalent, of (H_1), for example from 0.002 to 0.4 mole equivalent thereof, per mole of introduced diols $[(A_1) + (A_2)]$. The molar ratio $(E_{21})/[(A_1) + (A_2)]$ is then advantageously in the range from 0.01 to 1, preferably in the range from 0.02 to 0.5, particularly preferably in the range from 0.04 to 0.3. One mole equivalent of (H) is taken to mean one mole of (H) divided by the number of functional groups; in the case of the oligohydroxyl compounds (H_1), one mole equivalent of (H_1) is thus one mole of (H_1) divided by the number of its hydroxyl groups. These molar ratios apply to the specific non-ionic polyesters from the said starting components; if other and/or further components are used for the production of the polyesters or oligoesters, the molar ratios should, if necessary, be adjusted or changed correspondingly in order to obtain the corresponding polyester or oligoester properties. Through the reaction with (H), branched or optionally also dendromeric polyesters or oligoesters (P_S) can be produced.

The reaction is advantageously controlled in such a way that the average molecular weight \overline{M}_w of the polyesters produced is ≥ 1000 , and is preferably in the range from 1200 to 10^6 , particularly preferably in the range from 1500 to $3 \cdot 10^5$. The synthesis of the polyesters to be employed in accordance with the invention is advantageously carried out in such a way that the degree of polymerisation can be kept relatively low, in particular in such a way that oligoesters are formed.

Any anionic groups, in particular sulpho groups and/or carboxyl groups, present in the polyester (P_S) may be in the form of the free acid and if desired can be converted into a salt form by reaction with corresponding bases, where for the salt formation cations known per se, preferably hydrophilising cations, come into consideration, for example alkali metal cations (for example lithium, sodium or potassium) or ammonium cations {for example unsubstituted ammonium, mono-, di- or tri- $-(C_{1,2}\text{-alkyl})$ -ammonium, mono-, di- or tri- $-(C_{2,3}\text{-hydroxyalkyl})$ -ammonium, mono-, di- or tri- $-[(C_{1,2}\text{-alkoxy})(C_{2,3}\text{-alkyl})]$ -ammonium or morpholinium}, for which, for example, corresponding alkali metal hydroxides or carbonates, ammonia or the respective amines can be employed, preferably in the form of aqueous solutions.

The hydrophilicity of the products is controlled in such a way that the polyesters (P_S) produced are dispersible to colloiddally soluble in water (preferably self-dispersible to colloiddally soluble in water), i.e. that they give, in a concentration of from 0.1 to 30 % by weight, optionally with the assistance of suitable dispersants in an amount of up to 50 % by weight, based on (P_S) and optionally heating to above the melting point of (P_S), in water a corresponding 0.1 to 30 % (P_S) dispersion or colloidal

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solution or, for the self-dispersible to colloiddally soluble ones, even without the assistance of dispersants, give in water, through simple stirring-in and optionally heating to above the melting point of (P_S), an aqueous 0.1 to 30 % (P_S) dispersion or an aqueous 0.1 to 30 % colloidal (P_S) solution. A dispersion or colloidal solution of this type may be cloudy or translucent to transparent, but can in the latter case still be recognised through the Tyndall effect.

In polyesters and oligoesters (P_S) produced from terephthalic acid [as (B)], ethylene glycol and/or propylene glycol (GL) [as (A_1)] and polyethylene glycols [as (A_2)] and optionally (H) or (H_1) and end-capped with an oxyethylated alcohol [as (E_{21})], the hydrophilicity can also be estimated, for example, from the (GL)/(PEG) weight ratio, where (GL) denotes the proportion by weight of esterified ethylene glycol and/or propylene glycol and (PEG) denotes the proportion by weight of all esterified polyoxyethylene [from (A_2) and (E_{21})]. If the polyoxyethylene chains have an average molecular weight in the range from 500 to 5000, preferably from 800 to 3000, this (GL)/(PEG) weight ratio for the corresponding polyesters (P_S) is advantageously in the range from 1:3 to 1:60, preferably from 1:5 to 1:30. These values apply to the specific non-ionic polyesters from the said starting components; if other and/or further components are used for the production of the polyesters, the values should be adjusted or changed correspondingly in order to achieve the corresponding hydrophilicity.

Of the polyesters (P_S), preference is given to the polyesters (P_S'), i.e. those which are self-dispersible or colloiddally soluble in water, of these particularly the polyesters (P_S''), i.e. the non-ionic ones, especially (P_S''') those from the esterification or transesterification of (B_1) using (A_1), (A_{21}) and optionally (H_1) or (H_3) and end-capping with (E_{21}).

According to a particular embodiment of the invention, use is made as (P_S) of polyesters as are known as soil release agents for textile substrates (for example in detergents).

The polyesters (P_S) produced can be handled and used directly in the form in which they have been produced. They are advantageously used in the form of aqueous, preferably concentrated, compositions (W). These aqueous compositions (W) are dispersions or colloidal solutions of (P_S) and advantageously contain the polyesters (P_S) in a concentration in the range from 1 to 50 % by weight, preferably from 2 to 50 % by weight, particularly preferably from 3 to 25 % by weight. The aqueous compositions (W) can be simple aqueous dispersions or colloidal solutions of (P_S) alone or preferably contain further additives, in particular

(G) a thickening agent.

Suitable thickening agents (G) are preferably non-ionogenic and/or anionic substances which are known per se, in particular natural, modified or synthetic polymers. Examples of thickening agents (G) which can be employed are polysaccharides, polysaccharide derivatives and (co)poly(meth)acrylic acids and/or (co)poly(meth)acrylamides, for example xanthan gum, cellulose gum, guar gum, dextrans, gum arabic, carboxymethylcellulose, hydroxyethylcellulose, hydroxypropylcellulose, acrylyl-modified polysaccharides, copoly(meth)acrylic acids/(meth)acrylamides and optionally partially saponified poly(meth)acrylamides. Of these, preference is given to hydrophilic resins which are viscoelastic and preferably also pseudoplastic and non-thixotropic in aqueous solution, for example xanthan gum, cellulose gum, guar gum, dextrans, gum arabic, hydroxyethylcellulose, hydroxypropylcellulose and carboxymethylcellulose, or the said (meth)acrylic acid and/or (meth)acrylamide (co)polymers, of which particular preference is given to xanthan gum, homopolyacrylamides, copolyacrylamide-acrylic acid and partially saponified polyacrylamides. Advantageously, at least some of the acid groups, particularly the carboxylic acid groups, are in the form of salts (so that the respective products are water-soluble), for example as alkali metal salts (principally sodium salts). They can be employed as dry substance (for example as commercially available). If thickening agents (G) are employed, they are advantageously employed in such amounts that the viscosity of the aqueous concentrated compositions (W) [i.e. of the aqueous concentrated colloidal solutions or aqueous concentrated dispersions (W)] is $< 5000 \text{ mPa}\cdot\text{s}$, in particular at values $\leq 1000 \text{ mPa}\cdot\text{s}$, preferably in the range from 50 to $1000 \text{ mPa}\cdot\text{s}$. The concentration of thickening agent (G) in (W) is advantageously low, in particular lower than that of (P_S), and is, calculated as dry substance, for example $\leq 5 \%$ by weight, advantageously from 0 to 4 % by weight, preferably from 0.01 to 2 % by weight, particularly preferably from 0.1 to 1 % by weight.

If desired, the aqueous compositions (W) in addition to (P_S) and optionally (G), may contain further additives, in particular one or more of the following components:

- (X) a non-ionogenic or anionic surfactant or a mixture of non-ionogenic and/or anionic surfactants,
 - (Y) an agent for setting the pH
- and (Z) at least one formulation additive.

Suitable surfactants (X) are principally the following:

- (X_1) a non-ionogenic surfactant or a mixture of non-ionogenic surfactants, having an HLB ≥ 7 ,

and (X₂) an anion-active surfactant which is a carboxylic acid or sulphonic acid or a sulphuric acid partial ester or phosphoric acid partial ester or a salt thereof, or a mixture of such anion-active surfactants, having an HLB ≥ 7 ,

or mixtures of two or more of the surfactants (X₁) and (X₂), in particular at least one surfactant (X₁).

The surfactants (X₁) and (X₂) generally have dispersant character, in particular emulsifier character.

Suitable surfactants (X₁) are generally known compounds, essentially those having an emulsifier or dispersant character. Emulsifiers or dispersants of non-ionogenic character are known in large number in the art and are also described in the specialist literature, for example in M.J. SCHICK "Non-ionic Surfactants" (Volume 1 of "Surfactant Science Series", Marcel DEKKER Inc., New-York, 1967). Suitable non-ionogenic dispersants (X₁) are principally products of the oxyalkylation of fatty alcohols, fatty acids, fatty acid mono- or dialkanolamides (in which "alkanol" stands especially for "ethanol" or "isopropanol") or fatty acid partial esters of tri- to hexafunctional aliphatic polyols or, further, products of the interoxyalkylation of fatty acid esters (for example of natural triglycerides), where suitable oxyalkylation agents are C₂₋₄-alkylene oxides and optionally styrene oxide, and preferably at least 50 % of the introduced oxyalkylene units are oxyethylene units; advantageously at least 80 % of the introduced oxyalkylene units are oxyethylene units; particularly preferably all the introduced oxyalkylene units are oxyethylene units. The starting materials for the addition of the oxyalkylene units (fatty acids, fatty acid mono- or dialkanolamides, fatty alcohols, fatty acid esters or fatty acid polyol partial esters) can be any desired conventional products as used for the production of such surfactants, principally those having 9 to 24, preferably 11 to 22, particularly preferably 16 to 22, carbon atoms in the fatty radical. The fatty radicals may be unsaturated or saturated, branched or linear; mention may be made, for example, of the following fatty acids: lauric acid, myristic acid, palmitic acid, stearic acid, oleic acid, arachic acid and behenic acid, and technical-grade fatty acids, for example tallow fatty acid, coconut fatty acid, technical-grade oleic acid, tall oil fatty acid and technical-grade soya oil acid, and products of the hydrogenation and/or distillation thereof; examples of fatty acid mono- or dialkanolamides which may be mentioned are the mono- or diethanolamides or mono- or diisopropanolamides of said acids; fatty alcohols which may be mentioned are the derivatives of the respective fatty acids mentioned and synthetic alcohols, for example from the oxo synthesis, from the Ziegler process and/or from the Guerbet process [for example isotridecanols, Alfol grades (for example Alfol 10, 12 or 14) and 2-butyloctanol]. Partial esters of said polyols which may be mentioned are, for example, the mono- or difatty acid esters of glycerol, erythritol, sorbitol or sorbitan, in particular sorbitan mono- or dioleates or mono- or distearates. Of the said products, preference is

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given to the oxyalkylated fatty alcohols, especially the products of the oxyethylation of linear fatty alcohols, in particular those of the following average formula



in which R_1 signifies an aliphatic, linear hydrocarbon radical having 9 to 22 carbon atoms and p signifies from 4 to 40, or mixtures of such surfactants.

The HLB value of the surfactants (X_1) is advantageously in the range from 7 to 20, preferably in the range from 8 to 16. Of the compounds of the formula (II), particular preference is given to those in which R_1 contains 11 to 18 carbon atoms.

Suitable anion-active surfactants (X_2) are generally acids known per se (or salts thereof) having a surfactant character, as are usually employed as dispersants, for example as emulsifiers or as detergents. Such surfactant anionic compounds are known in the art and are described in large number in the specialist literature, for example in W.M. LINFIELD "Anionic Surfactants" (Volume 7 of "Surfactant Science Series", Marcel DEKKER Inc., New-York, 1976). Suitable anion-active surfactants are in particular those which contain a lipophilic radical (in particular the radical of a fatty acid or an aliphatic hydrocarbon radical of a fatty alcohol) which contains, for example, 8 to 24 carbon atoms, advantageously 10 to 22 carbon atoms, in particular 12 to 18 carbons, and may be aliphatic or araliphatic and where the aliphatic radicals may be linear or branched, saturated or unsaturated. In the case of carboxylic acids, the lipophilic radicals are preferably purely aliphatic, while in the case of sulphonic acids, the lipophilic radicals are preferably saturated purely aliphatic or araliphatic radicals. The carboxylic or sulphonic acid group may be bonded directly to the hydrocarbon radical (in particular as fatty acid, for example in the form of soaps, or as alkanesulphonic acid) or via a bridge which is interrupted by at least one heteroatom and is preferably aliphatic. Carboxyl groups can be introduced, for example, by oxidation of $-CH_2-OH$ groups, carboxyalkylation of hydroxyl groups or monoesterification of a hydroxyl group with a dicarboxylic anhydride, for example into such a molecule as described above as starting material for the oxyalkylation to give non-ionogenic surfactants or also of oxyalkylation products thereof, where the oxyalkylation can be carried out using oxiranes, principally ethylene oxide, propylene oxide and/or butylene oxide and optionally styrene oxide, and preferably at least 50 mol-% of the oxiranes employed is ethylene oxide; for example, these are products of the addition of from 1 to 12 mol of oxirane onto 1 mol of hydroxyl compounds, particularly as mentioned above as starting material for the oxyalkylation. The carboxyalkylation may be carried out using

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principally haloalkanecarboxylic acids, advantageously those in which the haloalkyl radical contains 1 to 4 carbon atoms, preferably 1 or 2 carbon atoms, halogen principally stands for chlorine or bromine, and the acid group can optionally be in salt form. A carboxyl group can also be introduced, for example, by monoesterification of an aliphatic dicarboxylic acid, for example by reaction of a hydroxyl compound with a cyclic anhydride, for example with phthalic anhydride or an aliphatic anhydride having 2 or 3 carbon atoms between the two carboxyl groups, for example succinic anhydride, maleic anhydride or glutaric anhydride. Phosphoric or sulphuric acid partial ester groups, for example, can also be introduced analogously by esterification. Suitable sulphonic acids are essentially products of the sulphonation of paraffins (for example produced by sulphochlorination or sulphoxidation), of α -olefins, of alkylbenzenes and of unsaturated fatty acids or alternatively formaldehyde condensates of sulphonated aromatic compounds (for example of sulphonated naphthalene). The anion-active surfactants are advantageously employed in the form of salts, where for salt formation hydrophilizing cations, in particular alkali metal cations (for example lithium, sodium, potassium) or ammonium cations [for example those mentioned above] or alternatively alkaline earth metal cations (for example calcium or magnesium), preferably come into consideration. Of the said anion-active surfactants (X_2), the ester group-free ones are preferred, principally soaps, in particular amine soaps, as well as the products of the carboxymethylation of oxyethylated fatty alcohols and the sulphonic acids, preferably in salt form as mentioned above, particularly as alkali metal salts.

The surfactants (X) are advantageously employed in amounts which are sufficient to enable (P_S) and, if used, (G) to be well dispersed in the aqueous phase and to enable a particularly stable aqueous colloidal solution or preferably dispersion of (P_S) and (G) to be formed.

The amount of (X) employed is advantageously ≤ 80 % by weight of (P_S), preferably ≤ 50 % by weight of (P_S), particularly preferably from 0 to 30 % by weight of (P_S). If (P_S) is self-dispersible to colloidally soluble [preferably (P_S')], (X) is not necessary.

Suitable as (Y) are any desired compounds known per se as are usually used for adjusting the pH of textile treatment agents, for example the above-mentioned bases, or alternatively buffer salts, such as, for example, sodium acetate or mono- or disodium phosphate, or occasionally also acids (for example a mineral acid, in particular hydrochloric acid or sulphuric acid, or a low-molecular-weight aliphatic acid, preferably having 1 to 4 carbon atoms, preferably formic acid, acetic acid or lactic acid).

The pH of the compositions (W) can vary widely and can optionally be adjusted, for example in the range from 3 to 10, preferably from 4 to 9, particularly preferably from 5 to 8, by addition of (Y).

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The compositions (W) may optionally additionally contain at least one formulation additive (Z), in particular (Z₁) an antifoam or (Z₂) an agent which inhibits bacterial growth or a microbicide, or (Z₃) a bleaching agent. As (Z₁), conventional antifoams can be employed, for example based on paraffins, mineral oil, fatty acid bisamides and/or hydrophobic silicic acid, for example commercial products, which can be employed in the concentrations recommended in each case. Suitable as (Z₂) are especially fungicides and bactericides, for example commercial products, which can be employed in the concentrations recommended in each case. As (Z₃), conventional bleaching agents can be employed, in particular reductive bleaching agents, such as, for example, sodium bisulphite. Suitable concentrations of (Z) are, for example, in the range from 0 to 4 % by weight, preferably from 0.001 to 2 % by weight, particularly preferably from 0.002 to 1 % by weight, based on (W).

Particularly worth of mention are the dispersions (W'), which essentially consist of (P_S) and water and optionally one or more of the additives (G), (X), (Y) and/or (Z) [for example of (P_S), (G) and water and optionally (X), (Y) and/or (Z)], particularly the dispersions (W''), which essentially consist of (P_S'), water and preferably (G) and in addition optionally one or more of the additives (Y) and/or (Z), particularly of (P_S'') or (P_S''') and water and preferably (G) and optionally one or more of the additives (Z₁), (Z₃) and/or (Y). Particularly preferred dispersions (W'') are e.g. those essentially consisting of (P_S''), water and at least one of the components (Z₂) and (G) and optionally (Y), or, where (P_S) is other than (P_S'), those essentially consisting of water, (P_S) and (X) and (Z₂) and optionally (G) and/or (Y).

The (G)- and/or X-containing compositions (W) according to the invention, in particular (W') and preferably (W''), can be produced in a very simple manner, by suitable mixing of the components, in particular by mixing (P_S), for example as a melt, in the presence of water, with (G) and/or (X), and optionally adding further additives, in particular one or more of (Y) and/or (Z).

The above-described polyesters (P_S), preferably in the form of aqueous compositions (W), are used as wet-acting lubricants for textile piece goods, i.e. as auxiliaries in the treatment of textile fabrics with treatment agents (T) (for example pre-treatment, dyeing, optical brightening or after-treatment) under conditions under which per se otherwise transport folds can form or friction can occur in or on the substrate, in particular in rope form or tubular form, where the compositions (W) to be employed in accordance with the invention serve particularly for preventing the stabilisation and marking of the folds formed during the treatment and for preventing damaging friction. Such processes are essentially exhaust processes from short liquor (liquor/substrate weight ratio, for example, in the range from 3:1 to 40:1, mostly from 4:1 to 20:1) – in particular in jet dyeing machines or in winch becks – under the

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treatment conditions and times which are usual per se (for example in the range from 20 minutes to 12 hours) as occur in particular in winch becks and especially in jet dyeing machines.

The aqueous compositions (W) or the polyesters (P_S), even in the presence of (G), have an optimum wet slippage behaviour, so that effective distribution on the surface of the wet fabric is possible on their use, after which they can be removed again, in general by discharging the liquid and/or by washing and/or rinsing operations as required by the process.

The treatment agents (T) are in general textile chemicals (in particular textile finishing chemicals) which can be removed from the substrate again for the part which is not fixed to the substrate, for example by washing and/or rinsing, after the respective treatment of the substrate.

As (T), the following sub-groups, in particular, are suitable:

(T₁) pre-treatment agents (principally wetting agents and detergents),

(T₂) main treatment agents (principally wetting agents, dyes, dyeing auxiliaries and optical brighteners),

and (T₃) after-treatment agents (principally finishing agents, detergents and reducing agents); where the respective treatments are carried out in aqueous medium.

Processes in which folds (i.e. transport folds) can form in the textile substrate are essentially taken to mean those in which the wet substrate tends to lie in folds during its transport in the dyeing machine, due to the action and possibly interference of various forces. The folds which form in such processes can per se result in marking of the crease points due to stabilisation during the treatment process, which can result in the disadvantages mentioned at the outset. In such processes, the polyesters (P_S) or the compositions (W) serve as wet-acting lubricants, in particular as agents for preventing transport folds, to the extent that they favour or facilitate slippage of the wet fabric or the wet folds and thus can prevent damaging stabilisation of the transport folds. Treatment processes which would per se cause transport folds are principally treatments on a winder (in particular in a winch beck) or especially in jet dyeing machines, in which the substrate is in each cycle fed over the winder or through the nozzle, at which point the fold formation and/or the forces acting on the folds, which can result in stabilisation of the folds, are the strongest.

Processes in which friction can take place in or on the textile substrate are essentially taken to mean those in which the wet substrate, during its transport in the dyeing machine, rubs against apparatus parts or adjacent substrate parts due to high running speed, passage through nozzles and/or a change in

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the transport direction and/or speed. The chafe points formed in such processes can result in marking thereof during the treatment process and in impairment of the physical properties of the substrate. In such processes, the polyesters (P_S) or the compositions (W) serve as wet-acting lubricants to the extent that they favour or facilitate slippage of the wet fabric (particularly on adjacent fabric or on metal) and thus can prevent damaging friction of the substrate. Possible treatment processes which would per se cause chafe points are principally treatments in jet dyeing machines, in which the substrate is in each cycle passed through the nozzle, at which point the relative acceleration and/or the forces acting on the substrate are the greatest, and in which the substrate is in each cycle pulled from its own position in the liquor toward the nozzle, so that the substrate-against-substrate acceleration or substrate-against-metal acceleration can at the respective points cause friction in places, which can result in the said chafe points.

Suitable substrates for the process according to the invention and for the wet-acting lubricants according to the invention are in general any desired substrates as can be employed in the said processes, principally those which contain synthetic fibres, especially polyester fibres, optionally in a blend with other fibres, in particular with other synthetic fibres (for example acrylic fibres or polyurethane fibres) or optionally modified natural fibres, for example of wool, silk or optionally modified cellulose (for example cotton, linen, jute, hemp, ramie, viscose rayon or cellulose acetate), where fibre blends that may be mentioned are, for example, polyester/cotton, polyester/polyacrylic, polyester/polyamide, polyester/polyurethane and polyester/cotton/polyurethane. The textile substrate can be employed in any desired form as piece goods, as can be treated in the processes mentioned, for example as tubular goods, as open textile webs or alternatively as semi-finished goods, essentially in rope form or tubular form, as is suitable for winders or especially in jet dyeing machines; both knitted goods and woven fabrics can be employed (for example fine to coarse simple knitted goods or interlocks, fine to coarse woven fabrics, terry goods, velvet and open-work and/or machine-embroidered textiles), in particular also goods made from microfibres, principally polyester microfibres and blends thereof with other correspondingly fine fibres.

The wet-acting lubricants according to the invention, i.e. polyesters (P_S) optionally in the form of aqueous compositions (W), in particular concentrated compositions (W), are advantageously employed in such concentrations that fold marking and chafe point formation are effectively prevented in the respective process. They are distinguished by their effectiveness and yield and can exhibit a very high action in very low concentrations; they are advantageously employed in concentrations which correspond to from 0.01 to 2 g of (P_S) per litre of liquor, preferably from 0.02 to 1 g of (P_S) per litre of liquor, particularly preferably from 0.04 to 0.5 g of (P_S) per litre of liquor.

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They can be produced in a simple and readily reproducible way, in particular as described above, and are also distinguished by the constancy of their properties – even in different lots – and the aqueous concentrated compositions (W) are distinguished by their stability to storage, shipment, transfer and pumping.

Since the wet-acting lubricants according to the invention, i.e. polyesters (P_S) or compositions (W), are also distinguished by their great independence from temperature variations and are substantially electrolyte-resistant, they can also be employed in a very wide selection of treatment conditions as occur for treatment with textile chemicals (T) in industry, in particular for pre-treatment with (T₁), for dyeing or optical brightening with (T₂) and for after-treatment with (T₃), for example with (T₁) during desizing or during bleaching, with (T₂) during dyeing or optical brightening or with (T₃) during after-treatment, but especially during dyeing or optical brightening. The dyeing or optical brightening can be carried out using any desired dyes or optical brighteners (T₂') and optionally dyeing auxiliaries (T₂'') which are suitable for the respective substrate and process and for the desired effect. For the dyeing of polyester-containing substrates, any desired corresponding dyes, for example disperse dyes, and optionally dyeing auxiliaries (for example carriers and/or levelling agents) can be employed, where the dyeing of substrates made from fibre blends, in particular made from cellulose fibres and synthetic fibres, can also be carried out using corresponding additional dyes, in particular reactive dyes, direct dyes, vat dyes or sulphur dyes (and optionally also corresponding dyeing auxiliaries). The processes can pass through any desired temperature regions as used for the respective substrate and the treatment agent employed and as a result of the apparatus and the desired purpose, for example from room temperature (for example at the beginning of dyeing) up to HT conditions (for example in the range from 102 to 180°C, in the closed apparatus). The electrolyte content of the liquors can also be as desired, as otherwise usually used for the respective process, for example corresponding to the alkali metal salt (for example sodium chloride or sodium sulphate) concentrations and/or alkali metal hydroxide or carbonate concentrations, as used in dyeing with said dyes, be it as a blend component in commercially available dye preparations and/or as uptake assistant in dyeing or optical brightening, or also as alkalis used in dyeing with sulphur dyes, vat dyes or reactive dyes.

The pH values can be as desired, as are suitable for the respective substrates, dyes and application processes. For polyester dyeings with dispersion dyes, suitable pH values are, for example, in the acidic region (for example in the pH range from 4 to 6, preferably from 4.5 to 5.5) or alternatively – with use of corresponding disperse dyes which are likewise suitable for alkaline dyeing – in the alkaline pH region (for example at pH > 8, principally in the pH range from 8.5 to 10).

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The polyesters (P_S) or compositions (W) are advantageously employed as wet-acting lubricants in dyeing or optical brightening, especially in jet dyeing machines (both those with hydrodynamic liquor transport and those with aerodynamic liquor transport), preferably for dyeing of polyester-containing substrates, particularly preferably of those essentially consisting only of polyester fibres (particularly also microfibres).

For use in the treatment of polyester fibres, particularly preferred polyesters or oligoesters (P_S) are polyesters or oligoesters (P_S'') in which the hydrophobic part originates from starting compounds (A_1) and (B_1) or is built up from monomer units which are directly homologous to (particularly ± 1 to 2 carbon atoms) or preferably identical with those originating or built up from the fibre polymer to be treated. Thus, if, for example, the polyester substrate to be treated is a polyester made from terephthalic acid and ethylene glycol (i.e. a polyethylene terephthalate), the hydrophobic part of (P_S) or (P_S'') preferably essentially consists of ester units made from terephthalic acid and ethylene glycol and/or propylene glycol, while the hydrophilic part then preferably essentially consists of (A_2), in particular a polyethylene glycol, and/or (E_{21}), which is then preferably a product of the addition of ethylene oxide onto a C_{1-18} -aliphatic alcohol, preferably a low-molecular-weight alkanol (particularly C_{1-4} -alkanol), and the polyester or oligoester (P_S) or (P_S'') optionally also contains as a constituent a copolymerised compound (H_1).

Due to the high resistance to temperature variations even at relatively high temperatures, the wet-acting lubricants according to the invention, i.e. polyesters (P_S) or respectively compositions (W), can be employed under the said conditions and optimally display their activity, without their action being impaired. Due to the high shear force stability of the wet-acting lubricants (W), particularly those which consist only of (P_S) and (G) and optionally (X), (Y) and/or (Z), in aqueous dispersion or colloidal solution, these are also particularly suitable as wet-acting lubricants in jet dyeing machines, especially also in those in which the goods or the liquor are subjected to extremely high dynamic stress, or in which very high shear forces develop in the liquor.

The compositions (W) or the polyesters (or oligoesters) (P_S) [in particular (P_S') or (P_S'') or even (P_S''')] have, even in very short liquors, for example at liquor/goods ratios of $\leq 15/1$, particularly also $\leq 10/1$, a very good, extremely superficial wet slippage action, in particular to the extent that they cause the lubricant to accumulate at the goods surface and the liquor to accumulate in the immediate vicinity of the lubricant and, as a flowing liquor layer, facilitates wet slippage of the goods to a surprisingly high degree.

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Through the use of the wet-acting lubricants (P_S) according to the invention, particularly in the form of their aqueous compositions (W), in particular optimally dyed and/or optically brightened materials may be obtained, in which the action of the respective treatment agent (pre-treatment agent, dye, optical brightener or after-treatment agent) is not impaired and an optimum goods appearance is obtained, even on use of very short liquors, even if almost all the liquor is on the goods during the process and almost no liquor remains over in the apparatus base.

The effectiveness of the polyesters (P_S) and the preparations (W) as wet-acting lubricants (or slip agents) can be determined, for example, as follows by measurement of the coefficient of friction: a first piece of fabric is tensioned in contact with the inside base of a shallow, flat trough; fixed at one end with a clamp and covered with an amount of liquor which corresponds to the liquor ratios which are usual in practice; a 200 g weight with a smooth, flat, rectangular base on which a second piece of the same fabric is tensioned and fixed is placed horizontally on top. The laid-on weight covered with the second piece of fabric (= "sledge") is then pulled in the longitudinal direction of the trough and of the first tensioned piece of fabric (= "track") until it starts moving and until it reaches a constant speed, and the traction force necessary to set the "sledge" in motion horizontally on the "track", starting from the end fixed with the clamp, and to move it horizontally in the traction direction at constant speed is determined. Both the static friction and the kinetic friction and thus both the static coefficient of friction and the kinetic coefficient of friction can thus be determined.

If N_0 denotes the normal force (i.e. the weight of the "sledge" on the "track"), Z_S denotes the horizontal traction force which is necessary to set the "sledge" in motion on the "track", and Z_K denotes the horizontal traction force which is necessary to keep the "sledge" moving at a constant speed on the "track", the static coefficient of friction μ_S can be expressed by the following formula

$$\mu_S = \frac{Z_S}{N_0}$$

and the kinetic coefficient of friction μ_K by the following formula

$$\mu_K = \frac{Z_K}{N_0}$$

Use of (P_S) allows not only μ_K but also μ_S to be reduced to very low values.

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The overall effectiveness of the wet-acting lubricants can be observed visually by checking the correspondingly treated goods in order to determine chafe points (or chafe marks) or transport fold marks (for example on a dyeing).

In the following examples, parts denote parts by weight and percentages denote percentages by weight; the temperatures are given in degrees Celsius. The products additionally added to the oligoesters in the examples (production, dispersion and application examples) are commercially available products. In the application examples, the dyes are employed in commercially available dry form with a pure dye content of about 25 % , the concentrations given relate to this form and are based on the substrate weight. C.I. stands for Colour Index.

Example 1

194.2 g of dimethyl terephthalate, 39.8 g of ethylene glycol, 96.6 g of 1,2-propylene glycol, 9.2 g of glycerol, 0.37 g of anhydrous sodium acetate and 0.19 g of titanium tetraisopropoxide are introduced into a four-necked flask with a capacity of 1 litre which is provided with stirrer, internal thermometer, gas-inlet tube and a 20 cm Vigreux column with Claisen bridge. The system is then rendered inert with nitrogen and heated to 165-167°C over the course of half an hour. The temperature is increased to 215-220°C over the course of a further 2.5 hours. The transesterification, and thus the distillation of methanol, commences at an internal temperature of about 165°C. After about 5 hours, more than 98 % of the expected amount of methanol has distilled off. The batch is cooled to 80°C, 72 g of methylpolyethylene glycol 750, 91.2 g of methylpolyethylene glycol 1820 and 387.5 g of polyethylene glycol 1500 are then added. The flask is again rendered inert and heated to 200-220°C, the pressure is then lowered to 1-5 mbar over the course of 1 hour, and the condensation is carried out at 220-240°C for a further 2-5 hours, during which a mixture of ethylene glycol and 1,2-propylene glycol distils off. After termination of the condensation, the system is aerated with nitrogen and cooled. The product solidifies on cooling to room temperature to give a solid material. Yield 730 g.

Further oligoesters are produced analogously to Example 1 using the following starting materials:

Example 2

194.2 g of dimethyl terephthalate
39.8 g of ethylene glycol
96.6 g of 1,2-propylene glycol

1.4 g of pentaerythritol
0.37 g of anhydrous sodium acetate
0.19 g of titanium tetraisopropoxide
72.0 g of methylpolyethylene glycol 750
91.2 g of methylpolyethylene glycol 1820
387.0 g of polyethylene glycol 1500.

Yield 725 g.

Example 3

145.6 g of dimethyl terephthalate
109.0 g of 1,2-propylene glycol
1.4 g of mannitol
0.28 g of anhydrous sodium acetate
0.14 g of titanium tetraisopropoxide
82.2 g of methylpolyethylene glycol 750
581.3 g of polyethylene glycol 3000.

Yield 800 g.

Example 4

194.2 g of dimethyl terephthalate
39.8 g of ethylene glycol
96.6 g of 1,2-propylene glycol
6.0 g of trimethylolethane
0.37 g of anhydrous sodium acetate
0.19 g of titanium tetraisopropoxide
54.0 g of methylpolyethylene glycol 750
68.4 g of methylpolyethylene glycol 1820
68.9 g of polyethylene glycol 1500
129.2 g of polyethylene glycol 800
258.3 g of polyethylene glycol 3000.

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Yield 760 g.

Example 5

223.3 g of dimethyl terephthalate
45.7 g of ethylene glycol
111.1 g of 1,2-propylene glycol
1.6 g of pentaerythritol
0.42 g of anhydrous sodium acetate
0.22 g of titanium tetraisopropoxide
28.2 g of methylpolyethylene glycol 750
35.7 g of methylpolyethylene glycol 1820
445.6 g of polyethylene glycol 1500.

Yield 720 g.

Example 6

213.5 g of dimethyl terephthalate
43.7 g of ethylene glycol
106.2 g of 1,2-propylene glycol
4.5 g of pentaerythritol
0.41 g of anhydrous sodium acetate
0.21 g of titanium tetraisopropoxide
39.6 g of methylpolyethylene glycol 750
50.2 g of methylpolyethylene glycol 1820
426.3 g of polyethylene glycol 1500.

Yield 720 g.

Example 7

174.7 g of dimethyl terephthalate
19.0 g of ethylene glycol
107.5 g of 1,2-propylene glycol

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3.3 g of trimethylolethane
0.33 g of anhydrous sodium acetate
0.17 g of titanium tetraisopropoxide
83.8 g of methylpolyethylene glycol 750
174.4 g of polyethylene glycol 1500
348.8 g of polyethylene glycol 3000.

Yield 765 g.

Example 8

194.2 g of dimethyl terephthalate
39.8 g of ethylene glycol
96.6 g of 1,2-propylene glycol
1.0 g of glycerol
0.37 g of anhydrous sodium acetate
0.19 g of titanium tetraisopropoxide
226.5 g of the adduct of 80 mol of ethylene oxide onto 1 mol of tallow fatty alcohol
387.5 g of polyethylene glycol 1500.

Yield 800 g.

Example 9

233.0 g of dimethyl terephthalate
47.7 g of ethylene glycol
115.9 g of 1,2-propylene glycol
8.1 g of 1,2,3-hexanetriol
0.44 g of anhydrous sodium acetate
0.23 g of titanium tetraisopropoxide
22.8 g of n-butylpolyethylene glycol 200
465.0 g of polyethylene glycol 1500

Yield 700 g.

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Example 10

291.2 g of dimethyl terephthalate
59.7 g of ethylene glycol
144.9 g of 1,2-propylene glycol
310.0 g of polyethylene glycol 800
123.3 g of methylpolyethylene glycol 750
0.6 g of anhydrous sodium acetate
0.3 g of titanium tetraisopropoxide

Yield 710g.

Dispersion W1

337 parts of water are initially introduced, and 2.0 parts of xanthan gum ("Kelzan" polysaccharide gum from Kelco Biopolymers) are added with stirring. After 6 hours, a colloidal solution is present, which is further diluted with 120 parts of water. 40 parts of the oligoester produced in accordance with Example 1, in molten form (65-70°C), are then drawn in under reduced pressure (residual pressure 300 mbar). A homogeneous, white, viscous dispersion forms which is stirred for a further 1 hour. The vacuum is then broken using nitrogen, and 1 part of biocide (1.5 % aqueous solution of a 1/1 mixture of 5-chloro-2-methyl-4-isothiazolin-3-one hydrochloride and 2-methyl-4-isothiazolin-3-one hydrochloride) is then added, the pH is adjusted to 7 (using sodium hydroxide solution or glacial acetic acid, depending on the water quality), and the product is then discharged.

Dispersion W2

The procedure is as described for dispersion W1, with the difference that instead of the oligoester from Example 1, the same amount of the oligoester from Example 2 is employed.

Dispersion W3

458.5 parts of water are initially introduced, and 0.5 parts of a partially hydrolyzed polyacrylamide (having an average molecular weight $\overline{M}_w = 20 \cdot 10^6$, with 27 ± 3 mol-% of $\text{CH}_2\text{-CH-COONa}$ monomer units) are added with stirring. As soon as a homogeneous solution is present (after about 12 hours), the mixture is heated to 50°C, and 50 parts of the oligoester produced in accordance with Example 2

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are added. A homogeneous, fine dispersion forms which is cooled to room temperature, and 1 part of the same biocide as in dispersion W1 is added. The product is subsequently discharged.

Dispersion W4

An 8 % aqueous dispersion of the oligoester produced in accordance with Example 3 is produced by initially introducing the water, drawing in the oligoester in molten form, and heating the mixture to 80°C with stirring, and, as soon as a homogeneous dispersion is present, cooling the dispersion to room temperature. Before discharge, 0.2 % of the same biocide as in dispersion W1 are added.

Dispersions W5 to W11

The procedure is as described for dispersion W1, with the difference that instead of the oligoester from Example 1, the same amount of the oligoester from each of Examples 4 to 10 is employed.

Dispersion W12

320.7 parts of ethylene glycol, 13.6 parts of diethanolamine and 12.9 parts of succinic anhydride are allowed to react at 60°C for 3 hours. 7.2 parts of potassium hydroxide and 334.5 parts of dimethyl terephthalate and 0.7 parts of manganese(II) acetate as catalyst are then added. The mixture is heated to 180°C under nitrogen, during which methanol and water distil off. The reaction melt obtained is cooled to 120°C, reacted with 646.5 parts of polyethylene glycol 750 monomethyl ether and re-heated to 180°C under reduced pressure. After 2 hours at 180°C, about 206.9 g of distillate are obtained. The mixture is then cooled to 120°C. About 1000 parts of melt at 120°C are obtained, which are added to a mixture of 3750 parts of water and 250 parts of the adduct of 10 mol of ethylene oxide onto 1 mol of oleyl alcohol at from 50 to 60°C. The mixture is subsequently cooled to room temperature. 5000 parts of aqueous dispersion W12 are obtained.

Application Example A [Dyeing of polyester in the jet (Mathis laboratory jet)]

A piece of polyester automobile velour is dyed as follows in a Mathis laboratory jet: 90 parts of polyester velour are introduced into the jet, which contains 900 parts of aqueous liquor and 1 g/l of dispersion W1. 0.62 % of C.I. Disperse Yellow 52, 2.3 % of C.I. Disperse Red 86, 0.5 % of C.I. Disperse Blue 77, 0.5 g/l of an anionic dispersant (formaldehyde condensate of sulphonated naphthalene) and 0.5 g/l of a levelling agent (mixture of sulphonated aromatic compounds) are added

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to the liquor, the pH is adjusted to from 4.5 to 5 with acetic acid, and the liquid is heated from room temperature to 130°C at a rate of 1°C/min, and dyeing is continued at 130°C for 30 minutes. The mixture is then cooled to 70°C, and the bath is discharged. 2 g/l of sodium hydrosulphite and 4 ml/l of 36°Bé sodium hydroxide are added in a fresh bath of 900 parts of water, the mixture is heated to 80°C and treatment is carried out, for reductive purification, at this temperature for a further 20 minutes. This is followed by re-cooling and rinsing twice with cold water. The liquor is then discharged, the goods are unloaded and dried in free air at room temperature. Dark-red, uniformly dyed goods having a homogeneous nap state and having a very attractive goods appearance are obtained.

Application Example B [Dyeing of polyester microfibre tricot in the jet (Mathis laboratory jet)]

A piece of polyester microfibre tricot is dyed as follows in a Mathis laboratory jet: 90 parts of polyester microfibre tricot are introduced into the jet, which contains 900 parts of aqueous liquor and 1 g/l of dispersion W1. 0.11 % of C.I. Disperse Yellow 52, 0.46 % of C.I. Disperse Red 86, 0.095 % of C.I. Disperse Blue 77 and 0.5 g/l of an anionic dispersant (formaldehyde condensate of sulphonated naphthalene) are added to the liquor, the pH is adjusted to from 4.5 to 5.0 with acetic acid, the liquor is heated from room temperature to 130°C at a rate of 1°C/min and dyeing is continued at 130°C for 15 minutes. This is followed by re-cooling and rinsing twice with water. The liquor is then discharged, the goods are unloaded and dried in free air at room temperature. Mouse-grey, uniformly dyed goods having a soft hand and a very attractive goods appearance are obtained.

Application Example C [Dyeing of polyester/viscose rayon blend fabric with dispersion dyes and reactive dyes in the jet (Mathis laboratory jet)]

100 parts of polyester/viscose rayon 70/30 blend fabric are introduced into 900 parts of an aqueous liquor, warmed to 50°C, which contains 1 parts of dispersion W1 and 60 parts of sodium sulphate (Glauber's salt). A solution of 0.35 parts of C.I. Reactive Blue 41 and 0.73 parts of C.I. Reactive Green 12 in 50 parts of water are added to the bath. After 20 minutes, a solution of 1.5 parts of soda in 50 parts of water are added, and dyeing is continued at 50°C for 20 minutes. A dispersion of 0.073 parts of C.I. Disperse Yellow 54 and 0.53 parts of C.I. Disperse Blue 60 in 50 parts of water is then added to the bath, and the pH of the bath is adjusted to 4.5-5.0 with acetic acid. The mixture is then heated from 50°C to 120°C at a rate of 1.5°C/min. The dyeing is carried out at 130°C for a further 45 minutes, and the bath is then cooled to 60°C at a rate of 2°C/min. After finishing in a conventional manner (rinsing, washing, drying), a very level green dyeing having a perfect goods appearance is obtained.

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The other Dispersions W2 to W12 are employed in the above Application Examples A, B and C in an analogous manner to Dispersion W1.

The results obtained in the above Application Examples A, B and C agree with the respective μ_s and μ_k values and their differences $\Delta\mu_s$ and $\Delta\mu_k$ against those of the blanks [i.e. with the same substrate and liquor, but without (W)].

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